# Total syntheses of (–)-Borrelidin and (–)-Doliculide and the development of the catalytic asymmetric addition of Grignard reagents to ketones

Madduri Venkata, Ashoka Vardhan Reddy

**Stellingen**

Behorende bij het proefschrift "Total syntheses of (–)-Borrelidin and (–)-Doliculide and the development of the catalytic asymmetric addition of Grignard reagents to ketones" van Ashoka V. R. Madduri.

1. When comparing the following papers, published in the same year: "*Stereoselective synthesis of pentose sugars under realistic prebiotic conditions*" by Pizzarello, S.; Weber, A. L. *Orig. Life Evol. Biosph.* **2010**, *40*, 3. & "*L-amino acids catalyze the formation of an excess of D-glyceraldehyde, and thus of other D sugars, under credible prebiotic conditions*" by Breslow, R.; Cheng, Z.-L. *Proc. Natl. Acad. Sci. USA,* **2010**, *107*, 5723, an in depth study brings to light that both papers deal with the same subject and lead to similar conclusions. Paradoxically, the Breslow paper cites the Pizzarello paper (ref 9) as follows: *"In the D sugars such as D-ribose or D-glucose or D-fructose other pieces are added to D-glyceraldehyde: a two-carbon piece to make D-ribose (9), a three-carbon piece to make D-glucose, etc...."* So it's highly unlikely that a reader unaware of the Pizzarello paper, will compare these two papers.

2. It is remarkable that the outcome of the biological activity study of a Spongistatin analogue, described by Smith *et al.* is not in accordance with the findings of Uckun *et al.*.

   Smith III, A. B.; Corbett, R. M.; Pettit, G. R.; Chapuis, J. -C.; Schmidt, J. M.; Hamel, E.; Jung, M. K. *Bioorg. Med. Chem. Lett.* **2002**, *12*, 2039.

   Uckun, F. M.; Mao, C.; Nikolay Vassilev, A. O.; Huang, H.; Jan, S. -T.; *Bioorg. Med. Chem. Lett.* **2000**, *10*, 541.

3. In their synthesis of Doliculide, Gosh *et al.* overlooked a partial racemization of the peptide fragment upon methylation of the nitrogen by NaH/MeI. Ghosh, A. K.; Liu, C. *Org. Lett.* **2001**, *3*, 635.
   Chapter 3 of this thesis.

4. The application of solubility differences between the pure enantiomer and the racemate of chiral phosphine ligands is currently underexplored.
   Chapter 6 of this thesis.

5. It should be considered unethical to submit results of same research on the same day to different journals.

   Uckun, F. M.; Mao, C.; Nikolay Vassilev, A. O.; Huang, H.; Jan, S. -T.; *Bioorg. Med. Chem. Lett.* **2000**, *10*, 541.

   Huang, H.; Mao, C.; Jan, S. -T.; Uckun, F. M. *Tetrahedron lett.* **2000**, *41*, 1699.

6. It is a misconception that organic chemists only get motivation from the fact that molecules or methods developed by them will help to cure cancer in the future.

7. In the next few years, the role of sodium borohydride and lithium aluminumhydride in organic synthesis will be taken over by catalytic hydrogenation.

8. A verse in Telugu "*Uppu kappurambu nokka polika nundu, Chooda chooda ruchulu jaada veru, Purushulandu punya purushulu veraya, Viswadhaabhiraama, Vinura Vema*". English translation: Salt and camphor look similar, but closer observation shows their taste is different. Likewise, among men virtuous people stand apart. Beloved of the bounteous, Vema, listen! –By Kumaragiri Vema Reddy, popularly known as Vemana (Telugu poet, Andhra Pradesh, India).